Fractal growth of silicon-rich domains during annealing of aluminum thin films deposited on silica

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We have investigated the reaction of aluminum on silica during annealing of aluminum thin films. We show that the oxidation of the aluminum is uniform, while the silicon migrates onto silicon-rich domains that have a fractal shape. We propose that the reaction is limited by diffusion of silicon in the film. [S1063-651X(96)02306-9]

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I. INTRODUCTION

When aluminum is in contact with silica, a reaction between the two materials, leading to the formation of alumina and silicon, can be thermally activated. The reaction can be summarized as

$$4\mathrm{Al}+3\mathrm{SiO_2}\rightarrow 2\mathrm{Al_2O_3}+3\mathrm{Si} \qquad (1)$$

and its formation $\Delta G^0=-225$ kCal. This reaction has long been studied and it has even been proposed [1] as a possible path for the production of silicon. Later, this reaction [2–7] was studied again because aluminum/silica interfaces are extensively used in electronics and because these interfaces were found not to be stable; more specifically Al-SiO_2-Si capacitors were shown to break down easily [4]. The reaction between aluminum and silica was also of interest in the context of composite materials [6] for tailoring of glass-fiber reinforced aluminum.

The spatiotemporal aspects of the reaction have not been thoroughly investigated, though some authors report that the annealing of aluminum thin films on silica leads to ''considerable roughening'' of the film [3]. It was also found that the evolution of the conductivity of the Al film on a SiO_2 substrate could not be modeled by a simple uniform oxidation of the aluminum film [3]. Finally, let us remark that two breakdown peaks of the SiO_2 film in Al-SiO_2-Si capacitors were attributed to ''the presence of small randomly distributed crystallized region'' and to ''quite massive defects'' [4]. Most importantly, no electrical shorts were observed on the areas that were not covered by the metal.

We have studied the reduction of silica by aluminum in the light of recent progress in the field of fractal or irregular growth [8–15], in particular diffusion limited aggregation (DLA) [15]. Our main conclusion is that the reaction of aluminum on silica involves nonequilibrium growth of irregular domains of a silicon-rich compound, which have escaped the previous studies, while the oxidation of the aluminum is uniform. This study provides insights into the kinetics of the reaction, which are complementary to the thermodynamical studies done so far [2–7].

II. EXPERIMENTS

Aluminum thin films were vapor deposited on soda-lime glass, on ceramic slides, and on silica slides [16,17]. Several Al thicknesses were studied, between 300 and 1000 Å . For control, similar films were deposited on alumina, copper, silicon, and gold. Most samples were annealed in a furnace under nitrogen flow (purity 5 ppm). The main series of samples were annealed at 400 °C for 2, 4, 8, 12, and 48 h. Other samples, especially the silica samples, were annealed at 550 °C and 620 °C for, respectively, 2 h and 10 min. Some samples were annealed under air. Some samples were annealed on a copper sample holder, at 500 °C, and some others were simply fired in a butane flame.

Initially, the aluminum film is uniform. After an annealing time of only 2 h in the furnace at 400 °C, spots about 5 μm in diameter appear on the Al film deposited on glass. They look like transparent irregular islands over a dark film (Fig. 1). Around the islands, the aluminum film retains a metallic silverish appearance, although it is somewhat tarnished. The number and size of the islands increase with the annealing time. After about 12 h (400 °C), the size of the islands is about 50 μm. The islands appear in scanning electron microscopy (SEM) as charged insulating domains (Fig. 2). When further metallized they were almost impossible to find with the SEM [18]. This is ascribed to the fact that the thickness of the islands is close to the thickness of the aluminum film. This is further confirmed by simultaneous scanning tunneling optical microsopy and atomic force microscopy (Fig. 3). Islands formed also in a few minutes on samples that were simply fired in a butane flame (temperature above 600 °C).

To reduce temperature gradients at the film surface we performed some experiments with the samples placed on top of a copper holder, with the aluminum film directly in contact with the copper surface. The result was a more uniform distribution of islands, but the island shape was similar.

No reaction was observed on the silicon, copper, and alumina substrates (control samples). Interestingly enough, a

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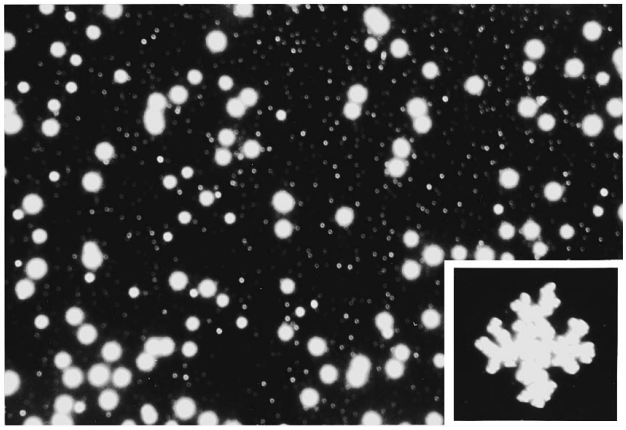

FIG. 1. Aluminum film deposited on glass, after an annealing time of 2 h at 400 °C. Bright spots appear on the film, which are easily observed with optical transmission microscopy (50×). Magnification 1500× of a bright spot, observed with transmission illumination.

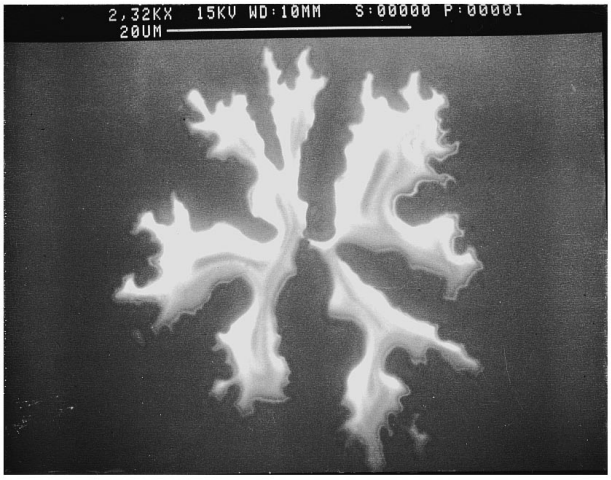

FIG. 2. In SEM, without metallizing the sample, the clusters appear as bright insulating domains. When they are further metallized, the patterns are almost invisible on the film.

reaction was observed between the aluminum and the silica *across* the gold coating on the gold control (which was a 1000-Å coating on top of a glass slide).

III. ANALYSIS OF THE SAMPLES

A. Morphology

The largest patterns were found on the ceramic samples annealed above 550 °C (Fig. 4) and on the silica samples annealed above 600 °C. A fractal analysis of these patterns was performed by the box counting method (on 16 patterns) at a magnification of 150×. Pictures were taken, then blown up, and scanned. The fractal analysis was performed on the scanned images with a resolution of 600×600 pixels. It revealed a fractal contour over two decades for the average patterns and slightly more than two decades for some of the largest patterns (Fig. 5). The fractal dimension of the patterns was found to be very close to the fractal dimension of DLA clusters: 1.66. A second set of patterns was studied. We considered smaller patterns (Fig. 6) at a magnification of 1000× and found again a fractal behavior between one and two decades, with the same exponent. The largest of all patterns was 2 mm. The patterns observed after a few minutes above 600 °C are fractals down to approximately the 5-μm scale. Note that the grain size in the Al film is much smaller (about 10 nm, obtained from x-ray-diffraction lines). To conclude this section, let us remark that up to several thousand DLA-like clusters can be obtained on a single sample of the size 1×1 cm^2.

B. Chemical analysis

1. X-ray studies

X-ray-diffraction analysis of the patterns was found to be extremely difficult due to the very small thickness of the films and to the localized nature of the patterns. X-ray diffraction demonstrated the existence of elemental silicon as a chemical product (data not shown), but no aluminum oxide could be detected. This confirms previous work by different authors [3–7], who, in the very same conditions, found evidence of elemental silicon while the presence of alumina was very hard to demonstrate, despite its being obvious. Some authors were able to find several phases of alumina, but after scratching and analyzing the product of the reaction of several samples [5–7].

2. Local EDX analysis

We performed an analysis by energy dispersive x ray (EDX) SEM of the samples on the soda lime glass (Fig. 7). This analysis gives a semiquantitative concentration map for the elements Si, Al, and O and also for impurities such as Ca, Na, and Mg. The x-ray photons counts revealed that the con-

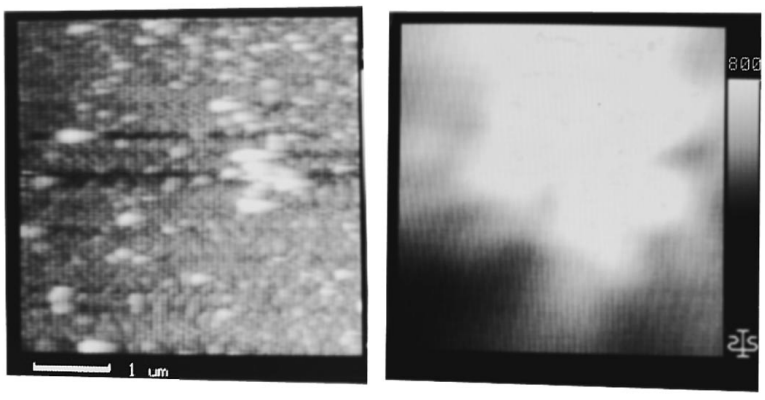

FIG. 3. When scanning the sample with atomic force microscopy (left) and near-field microscopy (right), one observes that, while the patterns are transparent, very little, if any, difference in topography is found. This is also observed in SEM and optical observations.

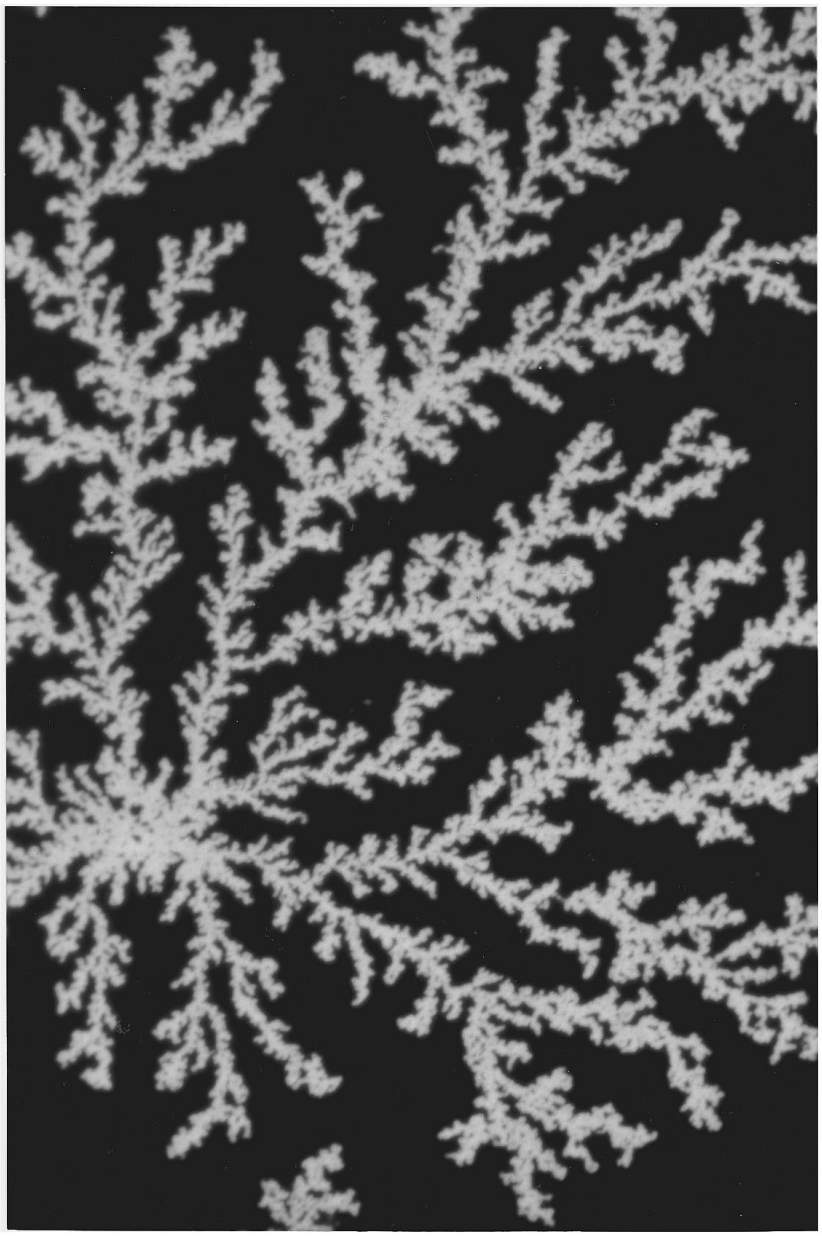

FIG. 4. The largest patterns were about 500 μm in size. One pattern was more than 1 mm in size. The largest patterns were found near the edges of ceramic samples annealed in the furnace at about 550 °C and also on samples fired in the flame. On silica, the largest patterns were found at temperatures above 600 °C.

centration of silicon is *much higher* in the growing clusters [Fig. 8(a)], while the concentration of aluminum is *smaller*. The aluminum peak in the film is found to be about five times as large as in the patterns [Fig. 8(b)]. The aluminum and silicon peaks are of comparable magnitude inside the patterns. The distribution of oxygen is found to be rather uniform through the patterns and in the surrounding aluminum film (data not shown). This analysis shows that the aluminum film that surrounds the fractal patterns is rather uniformly oxidized, despite its metallic appearance. The fractal patterns are silicon-rich clusters that have grown at the expense of the aluminum film (since there is very little change in topography). Further evidence that the aluminum film is uniformly oxidized comes from the color of the Al film surrounding the irregular clusters, which progressively loses its metallic appearance and becomes white and translucent (as observed *in situ* by transmission illumination).

The EDX analysis gives only semiquantitative results in part because the analysis is carried out over a sphere of ap-

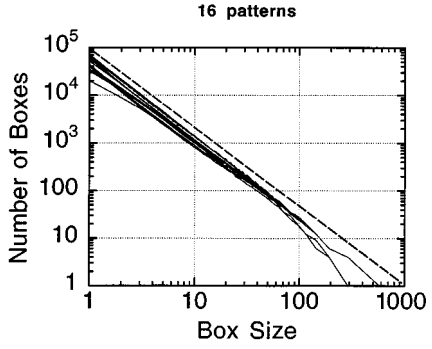

FIG. 5. Fractal analysis reveals a scaling behavior of the largest patterns over a little more than two orders of magnitude. Most patterns admit two orders of magnitude of fractality. In this figure the fractal dimension is calculated by the box-counting method on 16 patterns (picked up on the same sample, Al on Acticeram, temperature 550 °C, annealing time $\frac{1}{2}$ h).

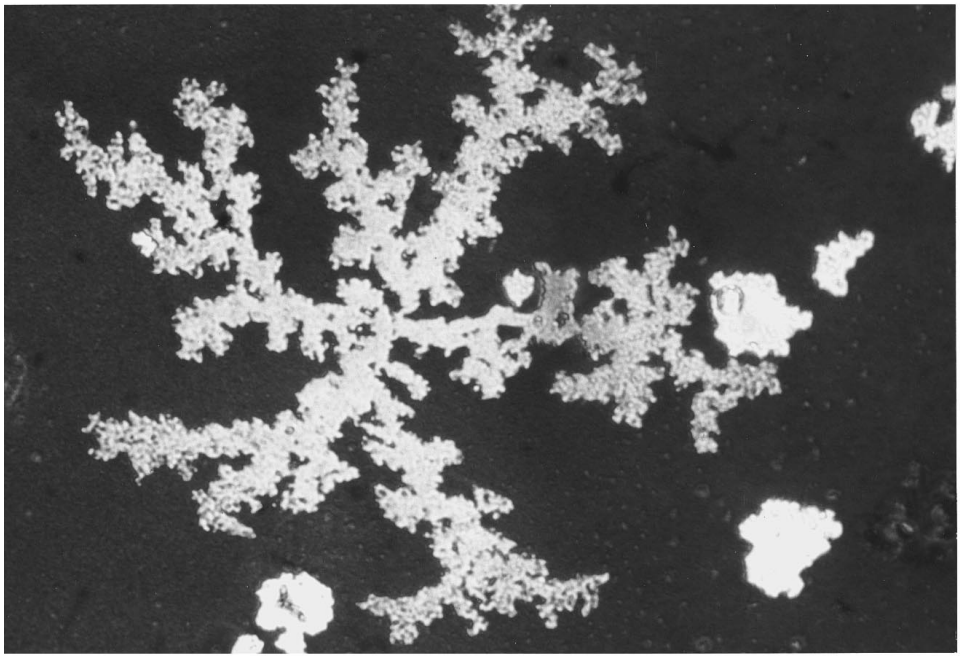

FIG. 6. Small clusters, at the magnification 1000×, after a short annealing time (ceramic, 550 °C). On these clusters the fractal behavior was found on somewhat less than two orders of magnitude. Note that these patterns are 20 times smaller than the clusters shown in Fig. 4. The white patches are 2D pores and small alumina pits.

proximately 1 μm. It is quite hard to determine the exact concentrations in a thin film that is only a fraction of a micrometer thick. The EDX measurements gave a concentration of silicon in the range 0–11 % in the aluminum film, while it gave an elemental concentration of silicon of about 25% in the DLA patterns, with some more concentrated pits at 70%. It might be possible that silicon is found in a crystallized form inside the patterns (hence the diffraction peak).

IV. DISCUSSION AND CONCLUSIONS

We now propose a mechanism for the creation of the fractal DLA-like silicon-rich domains based on existing studies [2–7] and on the previous results. Pabriputaloong and Piggott have demonstrated [7] that, during annealing, both oxygen and silicon are released in the film. From the uniformity of the aluminum oxidation that we observe, we conclude that the oxygen reacts almost immediately with the aluminum, forming alumina. Oxygen certainly does not diffuse in solid aluminum over a size comparable to the cluster size (say, 100 μm) and not even over a size comparable to the film thickness (about 0.1 μm), otherwise it would evaporate. Nor can diffusion of heat be responsible for the instability of the growth of the clusters, since no significant change in the cluster shape was found after performing the experiments on very conductive sample holders such as copper. We conclude that the main diffusing species in this experiment are elemental silicon and aluminum. A silicon-rich phase, as demonstrated by EDX and by optical microscopy, possibly pure silicon, nucleates on surface defects (which are often visible in the center of the patterns) or on the edges of the samples. The DLA shape of the clusters, whose overall

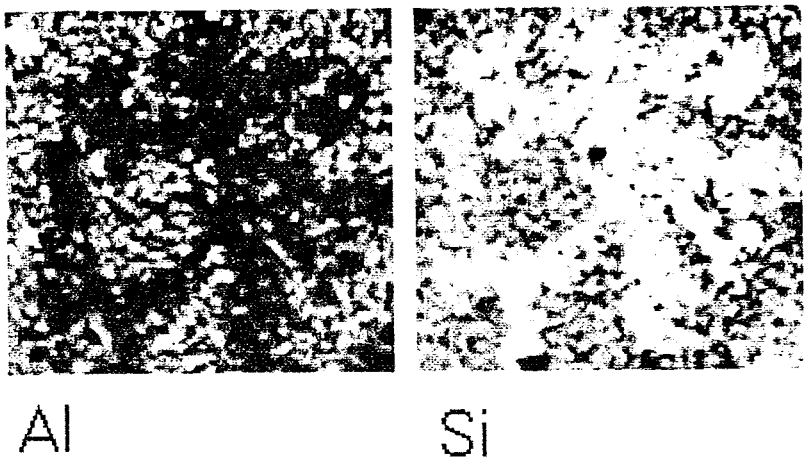

FIG. 7. EDX measurements of the concentration maps showing, qualitatively, the distribution of Si and Al. The oxygen map was found to be uniform (data not shown). One clearly observes that the patterns have a lower content of aluminum and a higher content of silicon than the rest of the film.

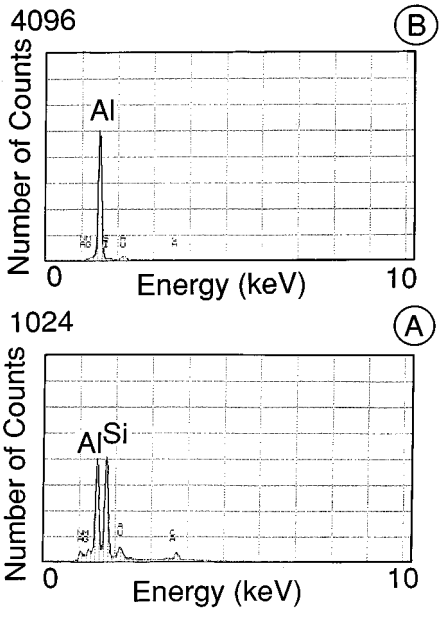

FIG. 8. (a) EDX data for the concentration of Si and Al inside a pattern. Al and Si appear in comparable concentrations. Note that there is a factor of 4 between the scale of these data and the data in (b). (b) EDX data for the concentration of Al and Si far from the patterns, in the film. The Al signal is very strong and the Si signal is weak. The Al peak inside the clusters is about 5 times weaker than the peak in the film.

gyration radius can be as large as several thousand times the film thickness, makes it very likely that the aggregate growth is limited by the two-dimensional (2D) diffusion of the silicon inside the film towards the clusters. In the range of temperatures that we have studied, the diffusion constant of Si in Al is in the range 10^{-10}–5×10^{-7} $cm^2 s^{-1}$ [19,20]. The sizes of the patterns at different temperatures and annealing times are compatible with the values of the corresponding diffusion lengths.

We observed that the patterns are more compact if the thickness of the aluminum film is reduced. This is easily explained in the frame of DLA growth. Indeed, if the thickness is reduced, one expects the equivalent ''concentration'' of silicon in the film to be larger. It has been shown by several authors that DLA growth in a finite concentration gives more compact clusters for higher concentrations [21–24]. Also, in the final stages of the annealing process, the fractal patterns become more compact. This is also easily explained in the context of DLA and related models [24–29]: when a constant external flux of diffusing monomers is added to a 2D DLA process, the patterns turn compact in the final stages of the aggregation process. A report on this effect will appear elsewhere [33].

In the SiO_2/Al system, and unlike other instances of quasi-two-dimensional DLA growth in a metallurgical context [30,31], a genuine chemical reaction provides the diffusing species. The experiment reported here suggests that similar chemical reactions could be observed on thin metal films reacting on silica. In particular, the very same experiment should be reproducible with magnesium or carbon instead of aluminum [32], and possibly iron.

Needless to say, the growth of fractal domains may be responsible for anomalies of the electrical response of Al/SiO_2 interfaces, which have been observed [4] and studied with the approximation of a continuous uniform aluminum film that gets thinner during the process. Figures 1–4,6,7 show why this assumption is very questionable. Also, the growth of fractal, instead of compact, domains may enhance the breakdown tendency of the Al-SiO_2-Si capacitors.

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[16] It is worth noting, in this context, that alumina is by far the most abundant impurity in glass and silica.
[17] The ceramic used was Acticeram, purchased from Préciver (Maisons-Alfort, France). Acticeram is a slowly crystallized glass that can sustain a temperature of 850 °C without deformation. We had only silica in the shape of tubes (diameter 1 cm), which were cut into segments.
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